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A STUDY OF THERMODYNAMIC BEHAVIOUR OF IMPERFECT GASES ASSUMING ASSOCIATION

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ABSTRACT. In this note the thermodynamic behaviour of an assembly of molecules of finite dimension which are associating and forming higher complex, has been investigated. The quasi-lattice theory of Dutta for real gases and ions in solution has been extended for investigating assemblies of associating and dissociating molecules and used here for calculating the isothermal compressibility. The result is in agreement with experience.

INTRODUCTION

In usual investigations of the properties and behaviour of perfect gases no consideration is taken for association of molecules. But for many real gases, such as N_2O_4, Iodine vapour, water vapour, sulphur vapour it has been found that association of molecules takes place in various degrees.

According to Fowler's idea (1936), the usual results of the imperfect gases can be obtained very easily by considering dissociation and association of molecules into higher complexes alone. From this idea, the behaviour of an assembly, composed of associating and dissociating molecules complexes like $X_1, X_2, \ldots X_n$ where X is the most elementary molecule, is investigated by the method of Fowler (Dutta, 1951). A deviation from the properties of a perfect gas is obtained but this deviation is not in the direction of imperfect gas. The isothermal compressibility, as obtained by Dutta, was greater than that of perfect gas. This result is justified from different considerations. It appears that a behaviour of imperfect gas cannot be obtained purely from association and dissociation if some of the usual causes of imperfection is not introduced. Here, by introduction of finite size of molecules, a deviation towards imperfection is obtained.

The quasilattice theory developed by Dutta (1953) is suitable for the discussion of various properties of gases where association and dissociation take place. Here, this quasi-lattice theory has been extended and used to deduce the equation of state of imperfect gases. After that the isothermal compressibility of the gas is calculated.

Now the imperfections of gases are due to two causes :

(i) finite size of the gas molecules or particles, and

(ii) presence of the fields of force. Here only the first cause i.e. the finite size of the particles, is taken into consideration.

Description of Assembly :

For the sake of simplicity, gas molecules are assumed to be present in their simplest form and in the form of second complex i.e., the molecules of this complex are formed by the association of two molecules of the gas. Then this system can be looked upon as a binary mixture of gases. In the assembly of the mixture it is assumed that N_1 is the average number of molecules of mass m_1 and N_2 is the average number of molecules of mass $m_2 = 2m_1$,

and $$N_1+2N_2 = N,$$

where N is the total number of molecules of the gas in the simplest form present in the assembly.

CALCULATION OF ENTROPY

In case of this binary mixture following quasi-lattice method and the principle of symmetrisation, the thermodynamic probability is given by,

$$W = [W_{12}\ W_{21}]^{\frac{1}{2}} \qquad \ldots (1)$$

where

$$W_{12} = \frac{(V/b_1)\ !}{N_1!(v/b_1-N_1)!} \cdot \frac{\left(\dfrac{V-N_1 b_{12}}{b_2}\right)!}{N_2!\left(\dfrac{v-N_1 b_{12}}{b_2}-N_2\right)!} \cdot \frac{N_1!}{\pi a_l!}\ \frac{N_2!}{\pi\, a'm!}$$

and W_{21} is a similar expression obtained by interchanging the suffices, 1 and 2 in the first two factors.

Here, the symbols have the same interpretation as in the papers of Dutta (1951)

Now, using Starling's approximation formula for factorials and taking usual variation of the logarithm of W,

subject to the conditions

$$\left.\begin{aligned} &\sum_1 \delta a_1 + 2\sum_m \delta a'_m = \delta N_1 + 2\delta N_2 = 0, \\ \text{and}\quad &\Sigma \epsilon_i \delta a_i + \sum_m \eta_m \delta a'_m + \chi \delta N_2 = 0 \end{aligned}\right\} \qquad \ldots (2)$$

where χ is the energy of association,

we get,

$$\frac{1}{2}\left\{\log\left(\frac{v}{b_1}-N_1\right)+\log\left(\frac{v-N_2 b_{12}}{b_1}-N_1\right)+\frac{b_{12}}{b_2}\log\left(1-\frac{N_2 b_2}{v-N_1 b_{12}}\right)\right\}$$

$$-\log a_i - \lambda - \mu\epsilon_i = 0$$

where λ and μ are Lagrange's multipliers.

From this, we have

$$a_i \cdot \frac{b_1}{v} \cdot e^{\frac{N_1 b_1 + N_2 b_{12}}{v}} = e^{-\lambda - \mu \varepsilon_i}$$

or,
$$a_i = \frac{v}{b_1} e^{-\lambda - \mu \varepsilon_i} \qquad \ldots (3)$$

(approximately)

and similarly

$$a_m' = \frac{v}{b_2} \cdot e^{-2\lambda - \mu(\eta_m + \chi)} \qquad \ldots (4)$$

According to Boltzmann hypothesis, and by equations (3) and (4) we get

$$S = k \log W_{max}$$

$$= k \left[\frac{1}{2} \left\{ \frac{v}{b_1} \log \frac{v}{b_1} - \left(\frac{v}{b_1} - N_1 \right) \log \left(\frac{v}{b_1} - N_1 \right) + \frac{v - N_1 b_{12}}{b_2} \log \left(\frac{v - N_1 b_{12}}{b_2} \right) \right.\right.$$

$$+ \left(\frac{v - N_1 b_{12}}{b_2} - N_2 \right) \log \left(\frac{v - N_1 b_{12}}{b_2} - N_2 \right) + \frac{v}{b_2} \log \frac{v}{b_2} + \left(\frac{v}{b_2} - N_2 \right) \cdot$$

$$\log \left(\frac{v}{b_2} - N_2 \right) + \left(\frac{v - N_2 b_{12}}{b_1} \right) \log \left(\frac{v - N_2 b_{12}}{b_1} \right) - \left(\frac{v - N_2 b_{12}}{b_1} - N_1 \right)$$

$$\left.\left. \log \left(\frac{v - N_2 b_{12}}{b_1} - N_1 \right) \right\} - N_1 \log v/b_1 - N_2 \log v/b_2 + N\lambda + \mu E \right] \qquad \ldots (5)$$

Now from the well known thermodynamic relation

$$\left(\frac{\partial S}{\partial E} \right) = 1/T,$$

we get
$$\frac{1}{T} = \mu k \quad \text{or,} \quad \mu = \frac{1}{kT} \qquad \ldots (6)$$

Again

$$N = N_1 + 2N_2 = \sum_1 a_i + 2\Sigma a' m.$$

$$= \sum_i \frac{v}{b_1} e^{-\lambda - \mu \varepsilon_i} + 2 \sum_m \frac{v}{b_2} e^{-2\lambda\mu - (\eta_m + \chi)}$$

$$= \frac{v}{b_1} e^{-\lambda} \frac{b_1}{h^3} \left(\frac{2\pi m_1}{\mu}\right)^{3/2} + \frac{2v}{b_2} e^{-2\lambda-\mu\chi} \frac{b_2}{h^3} \left(\frac{2\pi m_2}{\mu}\right)^{3/2}$$

or $$\frac{2N}{v} \cdot e^{\lambda} = \left(\frac{2\pi m_1}{\mu h^2}\right)^{3/2} \left[1+\sqrt{1+8e^{-\mu\chi}\left(\frac{\mu h^2}{\pi m_1}\right)^{3/2}\frac{N}{v}}\right]$$

or $$\lambda = \log v + \log\left\{\frac{1}{N}\left(\frac{2\pi m_1}{\mu h^2}\right)^{3/2}\right\} + \frac{2N}{V} e^{-\mu\chi}\left(\frac{\mu h^2}{\pi m_1}\right)^{3/2} \quad \ldots (7)$$

(upto first order).

EXPRESSIONS FOR OTHER THERMODYNAMIC FUNCTION

Now, from thermodynamics, we know

$$\psi = E - TS \quad \ldots (8)$$

and $$p = T\left(\frac{\partial \psi}{\partial V}\right)_{T,N} \quad \ldots (9)$$

So,

$$p = kT \cdot \left[-\frac{1}{2b_1}\left\{\log\left(1-\frac{N_1 b_1}{V}\right) + \log\left\{1-\frac{N_1 b_1}{V\left(1-\frac{N_2 b_{12}}{V}\right)}\right\}\right\}\right.$$

$$-\frac{1}{2b_2}\left\{\log\left(1-\frac{N_2 b_2}{V}\right) + \log\left\{1-\frac{N_2 b_2}{V\left(1-\frac{N_1 b_{12}}{V}\right)}\right\} - \frac{N_1+N_2}{V}\right.$$

$$\left.\left. + N\left\{\frac{1}{V} - \frac{2N}{V^2} e^{-\mu\chi}\left(\frac{\mu h^2}{\pi m_1}\right)^{3/2}\right\}\right]$$

or $$p = NkT\left[\frac{1}{V} + \frac{1}{V^2}\left\{(x_1^2\beta_1 + 2x_1x_2\beta_{12} + x_2^2\beta_2) - 2Ne^{-\mu\chi}\left(\frac{\mu h^2}{\pi m_1}\right)^{3/2}\right\}\right]$$

(upto first order of small quantities)

where

$$x_1 = \frac{N_1}{N}, \qquad x_2 = \frac{N_2}{N}$$

$$\beta_1 = \frac{1}{2} Nb_1, \quad \beta_{12} = \frac{1}{2} Nb_{12}, \quad \beta_2 = \frac{1}{2} Nb_2, \quad \ldots (10)$$

or $$p = \frac{NkT}{V}\left[1+\frac{B}{V}\right] = \frac{NKT}{V-B}\,. \qquad \ldots\ (11)$$

where $$B = \left\{(x_1^2\beta_1+2x_1x_2\beta_{12}+x_2^2\beta_2)-2Ne\,.\,^{\chi/KT}\left(\frac{h^2}{mmkT}\right)^{\frac{3}{2}}\right\}\Bigg]$$

The expression in the first bracket is same as that obtained by Lorentz (1927) and Dutta (1947), and the other term gives the effect of chemical reaction.

Isothermal compressibility.

From (11), we have

$$\text{isothermal compressibility} = -\frac{1}{V}\cdot\left(\frac{\partial V}{\partial p}\right)_T$$

$$= \frac{1}{p}(1-B/V)\,.$$

Now, by using (11), we can write

$$\frac{1}{V} = \frac{p}{NkT} - \frac{Bp^2}{NkT^2}\,.$$

(upto first order of small quantities)

and, so,

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p}\cdot\left[1-\frac{Bp}{NRT}\right]\left(\leqslant\frac{1}{p}\right) \qquad \ldots\ (12)$$

(upto first order of small quantities),

of course, if $B \geqslant 0$.

Thus, we get the isothermal compressibility of the assembly less than that of perfect gas provided the values of the characteristic constants of molecules like m_1, b_1, b_2, b_{12}, ... etc., of temperature and of association energy are suitable. This result is contrary to that obtained by Dutta (1951c) and is entirely due to the effect of exclusion volume.

CONCLUDING REMARKS

The investigations of the other thermodynamic behaviour of gas by the present method are interesting and those will be the subject-matter of future papers.

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REFERENCES

Dutta, M. 1951c : *Indian J. Phys.*, **35**, 319.
———— 1953 : *Proc. Nat. Inst. Sc. Ind.*, **19**, 183.
Fowler, R. H. 1936 : *Statistical Mechanics*, 2nd Edn., pp. 157-62, and 284-88.
Lorentz. H. 1927 : *Lectures in Theoretical Physics*, Vol. 2, Macmillan and Co., London.